



VERIFICATION OF TRANSLATION

Re : Japanese Patent Application No. 2002-184509

I, Miki HARIMA, of c/o Hosoda International Patent Office, OMM Building 5th Floor, P.O. Box 26, 1-7-31 Otemae, Chuo-ku, Osaka 540-6591, JAPAN, hereby declare that I am the translator of the documents attached and certify that the following is a true translation of the best of my knowledge and belief.

Dated this 13th day of January, 2006

A handwritten signature in cursive script, appearing to read "Miki Harima".

Miki HARIMA

JAPAN PATENT OFFICE

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Applicant(s): Kao Corporation

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Commissioner,

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Shinichiro OTA (Seal)

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[List of Annexed Documents]

[Document] Specification 1

[Document] Abstract 1

[Number of General Authorization] 0012367

[Requirement of Proof] Required

[Document] Specification

[Title of the Invention] Water-Based Ink

[Claims]

[Claim 1] A water-based ink comprising a colorant and a water-insoluble polymer having at least two hydroxyl groups at its end.

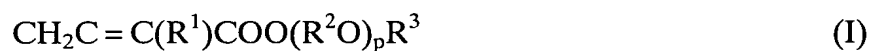
[Claim 2] The water-based ink according to claim 1, wherein the hydroxyl group of the water-insoluble polymer is derived from a chain transfer agent having at least two hydroxyl groups.

[Claim 3] The water-based ink according to claim 2, wherein the chain transfer agent is a mercapto-group containing chain transfer agent.

[Claim 4] The water-based ink according to any one of claims 1 to 3, wherein the colorant is a pigment and/or a dye.

[Claim 5] The water-based ink according to any one of claims 1 to 4, wherein the water-insoluble polymer is a water-insoluble vinyl polymer prepared by copolymerizing a monomer mixture comprising (A) a salt-forming group-containing monomer, (B) a macromer, and (C) a monomer copolymerizable with the salt-forming group-containing monomer and the macromer.

[Claim 6] The water-based ink according to claim 5, wherein the monomer mixture comprises at least one member selected from the group consisting of (D) a hydroxyl group-containing monomer, and (E) a monomer represented by the formula (I):



wherein R^1 is a hydrogen atom or a lower alkyl group having 1 to 5 carbon atoms; R^2 is a divalent hydrocarbon group having 1 to 30 carbon atoms which optionally has a hetero atom; R^3 is a hydrogen atom or a monovalent hydrocarbon group having 1 to 30 carbon atoms which may have a hetero atom; and p is a number of 1 to 60.

[Claim 7] The water-based ink according to any one of claims 2 to 6, wherein the chain transfer agent is 3-mercapto-1,2-propanediol or 1-thio- β -D-glucose.

[Claim 8] The water-based ink according to any one of claims 1 to 7, wherein the colorant is contained in particles of the water-insoluble polymer.

[Detailed Description of the Invention]

[0001]

[Technical Field to Which the Invention Pertains]

The present invention relates to a water-based ink. More specifically, the present invention relates to a water-based ink which can be suitably used for printers for inkjet printing.

[0002]

[Prior Art]

As coloring materials for water-based inks, aqueous dispersions containing a water-soluble dye or pigment have been used. Since the water-soluble dye has a wide range of color tones and is excellent in color reproducibility, the water-soluble dye has been used as a coloring material suitable for photographic printing. On the other hand, since a pigment-containing aqueous dispersion is excellent in weathering resistance, the pigment-containing aqueous dispersion has been used as a coloring material

which is suitable for a long-term storage of printouts and outdoor use.

[0003]

However, there are some disadvantages in using a water-soluble dye, such that the water-soluble dye is deteriorated in water resistance and light fastness, so that the water-soluble dye is likely to be blotted when printed on plain paper. Also, there are some disadvantages in using a pigment-containing aqueous dispersion, such that the pigment-containing aqueous dispersion has worsened fixing ability on paper surface, and deteriorated water resistance, rubbing resistance and high-lighter fastness when a surfactant or a water-soluble polymer is used as a dispersant in order to improve dispersion stability of the pigment. Furthermore, there is a disadvantage in using a pigment-containing aqueous dispersion, such that the pigment-containing aqueous dispersion is more likely to be blotted when printed on plain paper, although not so worse as the water-soluble dye.

[0004]

Therefore, recently, there have been proposed a technique of containing a polymer emulsion of a water-insoluble polymer in an ink, and a technique of incorporating a dye or pigment into a polymer emulsion.

[0005]

For instance, Japanese Patent Laid-Open Nos. Sho 54-058504, Hei 7-258591 and Hei 7-268260 describe the use of fine polymer particles into which a hydrophobic dye is incorporated in order to improve water resistance. Also, Japanese Patent Laid-Open No. 2000-239591 describes that a polymeric latex is added to an ink in order to improve rubbing resistance. Furthermore, Japanese Patent Laid-Open Nos. Hei 03-056573 and Hei 03-160069 describe that

fine polymer particles are added to an ink for the purpose of improving blotting resistance and fixing ability.

[0006]

However, there are some disadvantages in using these techniques such that jetting property when jetted with an inkjet printer is insufficient, so that the printouts are likely to become blurry, even though there are certain effects in water resistance, rubbing resistance and blotting resistance.

[0007]

Japanese Patent Laid-Open No. 2000-239591 describes that a specialized solvent is further added to an ink in order to improve its jetting property. However, when this solvent is added to the ink, the desired optical density may not be obtained. Therefore, this process is not necessarily effective from the viewpoint of quality of the printed characters.

[0008]

Japanese Patent Laid-Open No. Hei 03-56573 describes that fine polymer particles are cross-linked in order to prevent clogging of the nozzles. However, there are some disadvantages in using this technique, such that the ink fixing abilities such as rubbing resistance are insufficient, even though the cross-linking degree of the fine polymer particles is increased to a certain extent in order to sufficiently improve clogging of the nozzles.

[0009]

[Problems to Be Solved by the Invention]

An object of the present invention is to provide a water-based ink which is excellent in water resistance, high-lighter fastness and rubbing resistance, and also excellent in jetting property and blotting resistance when printed with an

inkjet printer.

[0010]

[Means to Solve the Problems]

The present invention relates to a water-based ink comprising a colorant and a water-insoluble polymer having at least two hydroxyl groups at its end.

[0011]

[Modes for Carrying out the Invention]

Since a water-insoluble polymer having at least two hydroxyl groups is used in the water-based ink of the present invention, the water-based ink is excellent in water resistance, high-lighter fastness and rubbing resistance, and also excellent in jetting property and blotting resistance when printed with an inkjet printer.

[0012]

The term “end” of the water-insoluble polymer as referred to herein means an end of the main chain of the water-insoluble polymer, not an end of the side chain of the water-insoluble polymer. However, when the water-insoluble polymer is a grafted copolymer, the term “end” of the water-insoluble polymer can include an end of a grafted chain.

[0013]

The end of the water-insoluble polymer may be an end derived from an initiator or a chain transfer agent, or an end derived from a monomer.

[0014]

A water-insoluble polymer having at least two hydroxyl groups at its end can be prepared, for instance, by using a chain transfer agent having at least two hydroxyl groups, a polymerization initiator and an iniferter (initiator-transfer

agent-terminator) having both functions of the chain transfer agent and the initiator during the polymerization of the polymer. When the chain transfer agent having at least two hydroxyl groups is used as described above, there is an advantage such that the jetting property becomes excellent when jetted with an inkjet printer.

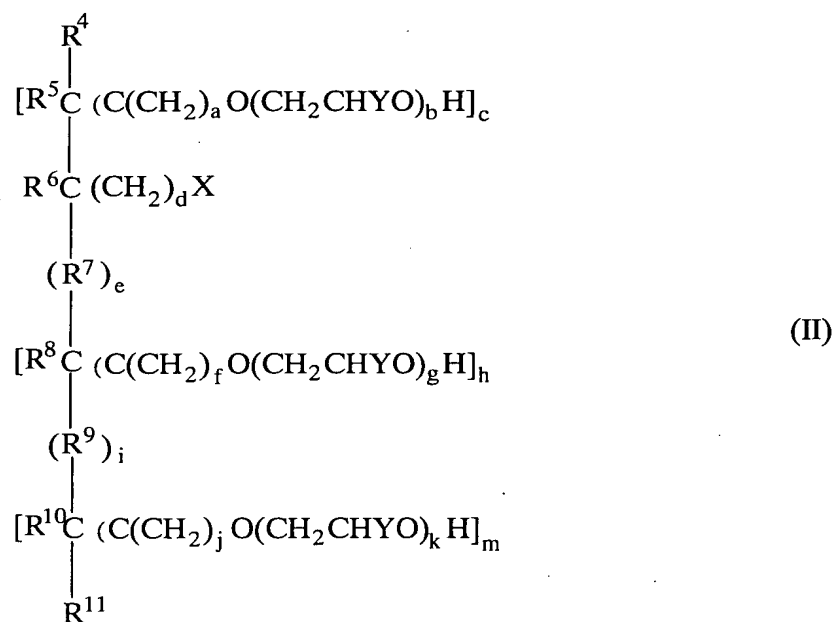
[0015]

Representative examples of the chain transfer agent having at least two hydroxyl groups include:

a mercapto-group containing chain transfer agent represented by the formula (II):

[0016]

[Ka 1]



[0017]

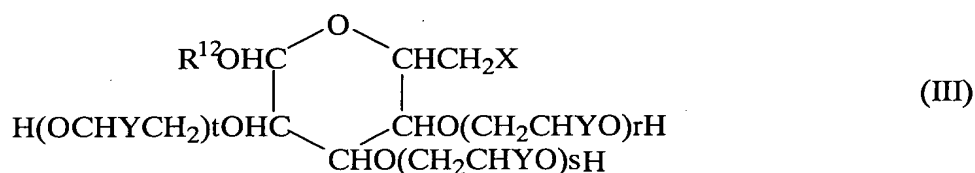
wherein each of R^4 , R^5 , R^6 , R^8 , R^{10} and R^{11} is independently a hydrogen atom,

$-C_nH_{2n+1}$, wherein n is an integer of 1 to 18, or $-C_nH_{2n}O(CH_2CHYO)_qH$, wherein Y is a hydrogen atom or methyl group, q is a number of 0 to 20, and n is as defined above; each of R^7 and R^9 is independently a hetero atom, $-C_nH_{2n-}$, wherein n is as defined above, or a divalent hydrocarbon group which optionally has a hetero atom; X is mercapto group; each of a , d , f and j is independently a number of 0 to 12; each of b , g and k is independently a number of 0 to 30; each of c , h and m is independently an integer of 1 to 5; and each of e and i is independently 0 or 1, with proviso that the total number of hydroxyl groups per molecule is at least 2;

a mercapto-group containing chain transfer agent represented by the formula (III):

[0018]

[Ka 2]



[0019]

wherein R^{12} is a hydrogen atom or $-C_nH_{2n+1}$, wherein n is as defined above; Y is as defined above; X is as defined above; each of r , s and t is independently a number of 0 to 30, with proviso that the total number of hydroxyl groups per molecule is at least 2; and the like. These chain transfer agents can be used alone or in admixture.

[0020]

The mercapto-group containing chain transfer agent represented by the

formula (II) includes, for instance, monomercapto-compounds of glycerol, diglycerol, triglycerol, tetraglycerol, trimethylolethane, trimethylolpropane, trimethylolbutane, 1,2,6-hexanetriol, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol, 2-methyl-2-(hydroxymethyl)-1,3-propanediol, pentaerythritol, erythritol, D-, L- and DL-threitol, adonitol, D- and L-arabitol, xylitol, dulcitol, L-iditol, D-mannitol and D-sorbitol. Among them, 3-mercapto-1,2-propanediol which is a monomercapto-compound of glycerol, 6-mercaptodiglycerol which is a monomercapto-compound of diglycerol, and a monomercapto-compound of pentaerythritol are preferable, and 3-mercapto-1,2-propanediol is more preferable, from the viewpoint of obtaining a water-based ink being excellent in jetting property.

[0021]

The mercapto-group containing chain transfer agent represented by the formula (III) includes, for instance, a monomercapto-compound of glucose, a monomercapto-compound of α -methylglucoside, a monomercapto-compound of β -methyl-D-alloside and the like. Among them, the monomercapto-compound of glucose is preferable, and specifically, 1-thio- β -D-glucose is more preferable, from the viewpoint of obtaining a water-based ink being excellent in jetting property.

[0022]

It is preferable that the amount of the chain transfer agent having at least two hydroxyl groups is 0.001 to 10 parts by weight based on 100 parts by weight of the entire monomers provided in the polymerization, from the viewpoint of obtaining a water-based ink being excellent in jetting property and from the viewpoint of dispersion stability. In addition, the amount of the chain transfer

agent having at least two hydroxyl groups is preferably 0.01 to 7 parts by weight, more preferably 0.1 to 5 parts by weight based on 100 parts by weight of the entire monomers provided in the polymerization from the viewpoint of the balance between water resistance, rubbing resistance, jetting property and blotting resistance.

[0023]

As the colorant, a pigment and/or a dye can be used.

The pigment can be any of an inorganic pigment and an organic pigment. The pigment can be used together with an extender as occasion demands.

[0024]

The inorganic pigment includes, for instance, carbon black, metal oxides, metal sulfides and the like. The carbon black includes furnace black, thermal lamp black, acetylene black, channel black, gas black and the like.

[0025]

The organic pigment includes azo pigments, diazo pigments, phthalocyanine pigments, quinacridone pigments, isoindolinone pigments, dioxazine pigments, perylene pigments, perinone pigments, thioindigo pigments, anthraquinone pigments, quinophthalone pigments and the like.

[0026]

When the pigment is used in a water-based ink, it is necessary to form stable fine particles in the ink by using a surfactant, a water-soluble polymer or a polymer insoluble to water as described below. Especially, it is preferable that the pigment is contained in the water-insoluble polymer particles described below from the viewpoints of water resistance, rubbing resistance, high-lighter fastness and blotting resistance.

[0027]

As the dye, a hydrophobic dye is preferable from the viewpoint of water resistance. Examples of the hydrophobic dye include an oil-soluble dye, a disperse dye, a basic dye and the like. Among them, the oil-soluble dye and the disperse dye are preferable from the viewpoint of color developability.

[0028]

The oil-soluble dye is not limited to specified ones, and includes, for instance, C.I. Solvent Black 3, 7, 27, 29 and 34; C.I. Solvent Yellow 14, 16, 29, 56 and 82; C.I. Solvent Red 1, 3, 8, 18, 24, 27, 43, 51, 72 and 73; C.I. Solvent Violet 3; C.I. Solvent Blue 2, 11 and 70; C.I. Solvent Green 3 and 7; C.I. Solvent Orange 2; and the like.

[0029]

The disperse dye is not limited to specified ones, and preferable examples of the disperse dye includes C.I. Disperse Yellow 5, 42, 54, 64, 79, 82, 83, 93, 99, 100, 119, 122, 124, 126, 160, 184:1, 186, 198, 199, 204, 224 and 237; C.I. Disperse Orange 13, 29, 31:1, 33, 49, 54, 55, 66, 73, 118, 119 and 163; C.I. Disperse Red 54, 60, 72, 73, 86, 88, 91, 93, 111, 126, 127, 134, 135, 143, 145, 152, 153, 154, 159, 164, 167:1, 177, 181, 204, 206, 207, 221, 239, 240, 258, 277, 278, 283, 311, 323, 343, 348, 356 and 362; C.I. Disperse Violet 33; C.I. Disperse Blue 56, 60, 73, 87, 113, 128, 143, 148, 154, 158, 165, 165:1, 165:2, 176, 183, 185, 197, 198, 201, 214, 224, 225, 257, 266, 267, 287, 354, 358, 365 and 368; C.I. Disperse Green 6:1; and the like.

[0030]

When the hydrophobic dye is used in a water-based ink, it is necessary to form stable fine particles in the ink by using a surfactant, a water-soluble

polymer or a polymer insoluble to water as described below. Especially, it is preferable that the hydrophobic dye is contained in the water-insoluble polymer particles from the viewpoints of water resistance, rubbing resistance, high-lighter fastness and blotting resistance. It is desired that the solubility of the hydrophobic dye in an organic solvent used for the preparation of the water-insoluble polymer at 25°C is at least 2 g/L, preferably 20 to 500 g/L from the viewpoint of efficiently incorporating the hydrophobic dye into the water-insoluble polymer.

[0031]

The water-insoluble polymer means a polymer having a solubility in 100 g of water at 25°C of less than 2 g when the salt-forming group of the polymer is neutralized at the time of dissolving the polymer in an organic solvent to prepare an aqueous dispersion of the water-insoluble polymer, and thereafter the aqueous dispersion is dried at 105°C for 2 hours.

[0032]

The solubility of the water-insoluble polymer contained in the aqueous dispersion of the water-insoluble polymer is determined by drying the aqueous dispersion at 105°C for 2 hours to remove a solvent to give a solid matter contained in the aqueous dispersion, and dissolving the solid matter in 100 g of water at 25°C.

[0033]

As the water-insoluble polymer, a water-insoluble vinyl polymer is preferable. As the water-insoluble vinyl polymer, a water-insoluble vinyl polymer prepared by copolymerizing a monomer mixture comprising (A) a salt-forming group-containing monomer [hereinafter referred to as component

(A)], (B) a macromer [hereinafter referred to as component (B)], and (C) a monomer copolymerizable with the salt-forming group-containing monomer and the macromer [hereinafter referred to as component (C)] is preferable.

[0034]

The component (A) includes a cationic monomer, an anionic monomer and the like. Examples of the component (A) include those described at page 5, column 7, line 24 to column 8, line 29 of Japanese Patent Laid-Open No. Hei 9-286939.

[0035]

Representative examples of the cationic monomer include unsaturated monomers having an amine group, unsaturated monomers having an ammonium salt group and the like. Among them, N,N-dimethylaminoethyl (meth)acrylate, N-(N',N'-dimethylaminopropyl) (meth)acrylamide and vinylpyrrolidone are preferable.

[0036]

Representative examples of the anionic monomer include unsaturated carboxylic acid monomers, unsaturated sulfonic acid monomers, unsaturated phosphoric acid monomers and the like. Among them, the unsaturated carboxylic acid monomers such as acrylic acid and methacrylic acid are preferable.

[0037]

The component (B) includes a macromer which is a monomer having a polymerizable unsaturated group and a number-average molecular weight of preferably 500 to 100000, more preferably 1000 to 10000. Among them, a styrenic macromer having a polymerizable functional group at one end is

preferable because of its high affinity for the colorant.

[0038]

The number-average molecular weight of the component (B) is determined by gel chromatography using chloroform containing 1 mmol/L dodecyldimethylamine as a solvent, with polystyrene as a standard substance.

[0039]

The styrenic macromer includes a styrene homopolymer having a polymerizable functional group at one end or a copolymer of styrene and other monomer, having a polymerizable functional group at one end. Among them, those having acryloyloxy group or methacryloyloxy group at one end as a polymerizable functional group are preferable. The content of styrene in the macromer is preferably at least 50% by weight, more preferably at least 70% by weight from the viewpoint of improving affinity for a colorant. The other monomer mentioned above includes acrylonitrile and the like.

[0040]

The component (C) includes, for instance, (meth)acrylates having an ester moiety of 1 to 30 carbon atoms, such as methyl (meth)acrylate, ethyl (meth)acrylate, (iso)propyl (meth)acrylate, (iso or tertiary)butyl (meth)acrylate, (iso)amyl (meth)acrylate, cyclohexyl (meth)acrylate, benzyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, (iso)octyl (meth)acrylate, (iso)decyl (meth)acrylate, (iso)dodecyl (meth)acrylate and (iso)stearyl (meth)acrylate; styrenic monomers such as styrene, vinyltoluene, 2-methylstyrene and chlorostyrene; and the like. These monomers can be used alone or in admixture of at least two kinds.

[0041]

Incidentally, the terms “(iso- or tertiary-)” and “(iso)” as referred to

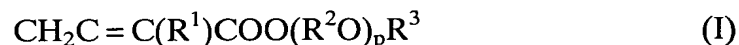
herein include both cases where these groups are present and where they are absent. In the case where these groups are absent, each of the listed compounds has a normal form. Also, “(meth)acrylate” means acrylate or methacrylate.

[0042]

It is preferable that the component (C) contains a styrenic monomer from the viewpoint of improvement in optical density and high-lighter fastness. As the styrenic monomer, styrene and 2-methylstyrene are preferable. These styrenic monomers may be used alone or in combination. In this case, the content of the styrenic monomer in the component (C) is preferably 10 to 100% by weight, more preferably 40 to 100% by weight from the viewpoint of improvement in optical density and high-lighter fastness.

[0043]

The monomer mixture may further contain at least one member selected from the group consisting of (D) a hydroxyl group-containing monomer [hereinafter referred to as component (D)], and (E) a monomer represented by the formula (I):



wherein R^1 is a hydrogen atom or a lower alkyl group; R^2 is a divalent hydrocarbon group having 1 to 30 carbon atoms which optionally has a hetero atom; R^3 is a hydrogen atom or a monovalent hydrocarbon group having 1 to 30 carbon atoms which optionally has a hetero atom; and p is a number of 1 to 60 [hereinafter referred to as component (E)].

[0044]

The component (D) exhibits some excellent effects such as increase of dispersion stability and improvement of high-lighter fastness in a short period of time during printing.

[0045]

The component (D) includes, for instance, 2-hydroxyethyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, polyethylene glycol($n=2$ to 30), (meth)acrylate, poly(ethylene glycol($n=1$ to 15)-propylene glycol($n=1$ to 15)) (meth)acrylate and the like. Among them, 2-hydroxyethyl (meth)acrylate is preferable.

[0046]

The component (E) exhibits some excellent effects such as increase of jetting stability of a water-based ink and suppression of the generation of crookedness even in continuous printing.

[0047]

In the formula (I), R^1 is a hydrogen atom or a lower alkyl group having 1 to 5 carbon atoms.

[0048]

R^2 is a divalent hydrocarbon group having 1 to 30 carbon atoms which optionally has a hetero atom. The hetero atom includes, for instance, nitrogen atom, oxygen atom, a halogen atom and sulfur atom.

[0049]

Representative examples of R^2 include an aromatic ring having 6 to 30 carbon atoms which optionally has a substituent; a heterocyclic ring having 3 to 30 carbon atoms which optionally has a substituent; and an alkylene group having 1 to 30 carbon atoms which optionally has a substituent. These rings or

groups may be used in combination of at least two kinds. The substituent includes an aromatic ring having 6 to 29 carbon atoms, a heterocyclic ring having 3 to 29 carbon atoms, an alkyl group having 1 to 29 carbon atoms, halogen atoms, amino group and the like.

[0050]

Preferred examples of R^2 include a phenylene group which optionally has a substituent of 1 to 24 carbon atoms; an aliphatic alkylene group having 1 to 30 carbon atoms, preferably 1 to 20 carbon atoms; an aromatic ring-containing alkylene group having 7 to 30 carbon atoms; and a heterocyclic ring-containing alkylene group having 4 to 30 carbon atoms.

[0051]

Preferred examples of the R^2O group include an oxyalkylene group having 2 to 7 carbon atoms, such as oxyethylene group, oxy(iso)propylene group, oxytetramethylene group, oxyheptamethylene group, oxyhexamethylene group and a combination of at least one member of these oxyalkylenes; and oxyphenylene group.

[0052]

R^3 is a monovalent hydrocarbon group having 1 to 30 carbon atoms which optionally has a hetero atom. The hetero atom includes, for instance, nitrogen atom, oxygen atom and sulfur atom.

[0053]

Representative examples of R^3 include an aromatic ring having 6 to 30 carbon atoms which optionally has a substituent; a heterocyclic ring having 3 to 30 carbon atoms which optionally has a substituent; or an alkyl group having 1 to 30 carbon atoms which optionally has a substituent. The substituent includes

an aromatic ring having 6 to 29 carbon atoms, a heterocyclic ring having 4 to 29 carbon atoms, halogen atoms, amino group and the like.

[0054]

Preferred examples of R^3 include phenyl group, an aliphatic alkyl group having 1 to 30 carbon atoms, preferably 1 to 20 carbon atoms, an aromatic ring-containing alkyl group having 7 to 30 carbon atoms, and a heterocyclic ring-containing alkyl group having 4 to 30 carbon atoms.

[0055]

More preferable examples of R^3 include alkyl groups having 1 to 6 carbon atoms, such as methyl group, ethyl group, (iso)propyl group, (iso)butyl group, (iso)pentyl group and (iso)hexyl group; phenyl group; and the like.

t[sic] is a number of 1 to 60, especially preferably a number of 1 to 30.

[0056]

Concrete examples of the component (E) include methoxypolyethylene glycol (1-30: showing the value of p in the formula (I), hereinafter referred to the same) (meth)acrylates, methoxypolytetramethylene glycol (1-30) (meth)acrylates, ethoxypolyethylene glycol (1-30) (meth)acrylates, (iso)propoxypolyethylene glycol (1-30) (meth)acrylates, butoxypolyethylene glycol (1-30) (meth)acrylates, methoxypolypropylene glycol (1-30) (meth)acrylates, methoxy(ethylene glycol-propylene glycol copolymer) (1-30, out of which ethylene glycol: 1-29) (meth)acrylates and the like. These monomers can be used alone or in admixture of at least two kinds. Among them, the methoxypolyethylene glycol (1-30) (meth)acrylates are preferable.

[0057]

The content of the component (A) in the water-insoluble vinyl polymer is

preferably 1 to 50% by weight, more preferably 2 to 40% by weight from the viewpoint of dispersion stability of the resulting dispersion.

[0058]

The content of the component (B) in the water-insoluble vinyl polymer is preferably 1 to 25% by weight, more preferably 5 to 20% by weight especially from the viewpoint of dispersion stability of the fine polymer particles containing a colorant.

[0059]

The content of the component (C) in the water-insoluble vinyl polymer is preferably 5 to 98% by weight, more preferably 10 to 60% by weight from the viewpoints of water resistance, rubbing resistance, high-lighter fastness and bleeding resistance.

[0060]

The content of the component (D) in the water-insoluble vinyl polymer is preferably 5 to 40% by weight, more preferably 7 to 20% by weight from the viewpoints of jetting stability, optical density and high-lighter fastness.

[0061]

The total content of the component (A) and the component (D) in the water-insoluble polymer is preferably 6 to 60% by weight, more preferably 10 to 50% by weight, from the viewpoints of stability in water and water resistance.

[0062]

The content of the component (E) in the water-insoluble vinyl polymer is preferably 5 to 50% by weight, more preferably 10 to 40% by weight from the viewpoints of jetting stability and dispersion stability.

[0063]

The total content of the component (A) and the component (E) in the water-insoluble vinyl polymer is preferably 6 to 75% by weight, more preferably 13 to 50% by weight from the viewpoints of dispersion stability in water and jetting stability.

[0064]

The total content of the component (A), the component (D) and the component (E) in the water-insoluble vinyl polymer is preferably 6 to 60% by weight, more preferably 7 to 50% by weight from the viewpoints of dispersion stability in water and jetting stability.

[0065]

The water-insoluble vinyl polymer can be prepared by copolymerizing a monomer mixture by a known polymerization method such as a bulk polymerization method, a solution polymerization method, a suspension polymerization method or an emulsion polymerization method. Among these polymerization methods, the solution polymerization method is preferable.

[0066]

The solvent used in the solution polymerization method is not limited to specified ones, and a polar organic solvent is preferable. The polar organic solvent can also be used in admixture with water. The polar organic solvent includes, for instance, aliphatic alcohols having 1 to 3 carbon atoms, such as methanol, ethanol and propanol; ketones such as acetone and methyl ethyl ketone; esters such as ethyl acetate; and the like. Among them, methanol, ethanol, acetone, methyl ethyl ketone or a liquid mixture of the solvent and water is preferable.

[0067]

A radical polymerization initiator can be used in the polymerization.

As the radical polymerization initiator, azo compounds such as 2,2'-azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile), dimethyl-2,2'-azobisbutyrate, 2,2'-azobis(2-methylbutyronitrile) and 1,1'-azobis(1-cyclohexanecarbonitrile) are preferable. Also, there can be used organic peroxides such as t-butyl peroxyoctoate, di-t-butyl peroxide and dibenzoyl oxide.

[0068]

The amount of the radical polymerization initiator is preferably 0.001 to 5% by mole, more preferably 0.01 to 2% by mole in the monomer mixture.

[0069]

The conditions for polymerizing the monomer mixture differ depending upon kinds of the radical polymerization initiator, monomers and solvent used, and the like. Usually, the polymerization temperature is 30° to 100°C, preferably 50° to 80°C, and the polymerization time is 1 to 20 hours. It is preferable that the atmosphere for polymerization is an atmosphere of an inert gas such as nitrogen gas.

[0070]

After termination of the polymerization reaction, the water-insoluble vinyl polymer can be isolated from the reaction solution by a known method such as re-precipitation or solvent distillation. Also, the resulting water-insoluble vinyl polymer can be purified by removing unreacted monomers and the like therefrom by repeat of re-precipitation, membrane separation, a chromatographic method, an extraction method or the like.

[0071]

It is preferable that the weight-average molecular weight of the water-insoluble vinyl polymer is 3000 to 100000 from the viewpoints of water resistance, rubbing resistance, high-lighter fastness and dispersion stability after printing.

[0072]

As the neutralizing agent for the water-insoluble vinyl polymer, an acid or a base can be used in accordance with the kind of the salt-forming group of the polymer. The acid includes inorganic acids such as hydrochloric acid and sulfuric acid; and organic acids such as acetic acid, propionic acid, lactic acid, succinic acid, glycollic acid, gluconic acid and glyceric acid. The base includes amines such as trimethylamine, triethylamine, diethanolamine, N-methyldiethanolamine and triethanolamine; ammonia; alkali metal hydroxides such as sodium hydroxide and potassium hydroxide; and the like.

[0073]

The neutralization degree is not limited to specified ones. It is preferable that the resulting aqueous dispersion is usually neutral, for instance the pH of the aqueous dispersion is 4.5 to 9.5.

[0074]

After the neutralization of the water-insoluble vinyl polymer, the water-insoluble vinyl polymer can be solely contained in the ink. Alternatively, particles of the water-insoluble vinyl polymer containing a colorant can be contained in the ink. Among them, the particles of the water-insoluble vinyl polymer containing a colorant are preferable from the viewpoint of satisfying all of water resistance, high-lighter fastness, rubbing resistance, jetting property and blotting resistance.

[0075]

The content of the water-insoluble polymer in the ink is 0.05 to 20 parts by weight, preferably 0.1 to 10 parts by weight, more preferably 0.5 to 5 parts by weight based on 100 parts by weight of the ink from the viewpoints of water resistance, rubbing resistance, high-lighter fastness, jetting property and bleeding resistance.

[0076]

As the process for obtaining an aqueous dispersion of pigment-containing water-insoluble polymer particles, a process comprising dissolving the water-insoluble polymer in an organic solvent; adding a pigment, water and a neutralizing agent, and a surfactant as occasion demands to the resulting solution; kneading the mixture to form a paste; diluting the paste with water as occasion demands; and distilling off the organic solvent to make it into a water-based system, is preferable.

[0077]

In addition, an aqueous dispersion of hydrophobic dye-containing water-insoluble polymer particles can be prepared by a known emulsification process. For instance, the aqueous dispersion can be obtained by dissolving a water-insoluble polymer and a hydrophobic dye in an organic solvent; adding a neutralizing agent to the resulting solution as occasion demands to ionize the salt-forming group of the polymer; adding water thereto; dispersing the mixture using a disperser or a ultrasonic emulsifier as occasion demands; and thereafter distilling off the organic solvent to phase-invert into a water-based system.

[0078]

The amount of the colorant in the water-insoluble polymer particles is

preferably 20 to 1000 parts by weight, more preferably 40 to 800 parts by weight, even more preferably 60 to 600 parts by weight based on 100 parts by weight of the solid content of the water-insoluble polymer from the viewpoints of increasing optical density, facilitating the incorporation of the colorant into the polymer particles and improving water resistance, rubbing resistance and high-lighter fastness.

[0079]

The average particle diameters of the water-insoluble polymer particles and the water-insoluble polymer particles containing the colorant are determined in accordance with the method described in the following Preparation Examples. It is preferable that each of the average particle diameters is 10 to 500 nm from the viewpoint of dispersion stability.

[0080]

The content of the colorant in the ink is not limited to specified ones as long as satisfactory optical density can be obtained. Usually, the content is preferably 1 to 30% by weight, more preferably 2 to 10% by weight, even more preferably 4 to 8% by weight from the viewpoint of giving satisfactory jetting stability and optical density.

[0081]

There can be added various additives, for instance, a wetting agent such as polyhydric alcohols, a dispersant, a defoaming agent, a mildewproof agent, a chelating agent, a pH adjusting agent and the like to the water-based ink of the present invention.

[0082]

[Examples]

Preparation Examples 1 to 5 (Preparation of Polymer Solutions)

A reaction vessel was charged with 30 parts by weight of methyl ethyl ketone, monomers and a chain transfer agent in the kinds and amounts listed in the column of "Initially Charged Monomers" of Table 1, and nitrogen gas substitution was sufficiently carried out.

[0083]

On the other hand, a dropping funnel was charged with monomers, a chain transfer agent in the kinds and amounts listed in the column of "Dropping Monomers" of Table 1, 70 parts by weight of methyl ethyl ketone, and a solution prepared by dissolving 0.1 parts by weight of 2,2'-azobis(2,4-dimethylvaleronitrile) in 5 parts by weight of methyl ethyl ketone, and the mixture in the dropping funnel was added dropwise to the reaction vessel to polymerize the mixture at 70°C for 5 hours. Thereafter, the resulting mixture was aged at 75°C for 10 hours, to give a polymer solution.

[0084]

A part of the resulting polymer solution was dried under reduced pressure at 105°C for 2 hours and isolated by removing the solvent therefrom. The weight-average molecular weight of the polymer was determined by gel permeation chromatography using polystyrene as a standard substance and chloroform containing dodecyldimethylamine of 1 mmol/L as a solvent. As a result, the polymer had a weight-average molecular weight as shown in Table 1.

[0085]

Each name listed in Table 1 means the followings:

- Styrenic macromer: commercially available from TOAGOSEI CO., LTD. under the trade name of AS-6 (styrene homopolymerized macromer having a

polymerizable functional group of methacryloyloxy group at one end,
number-average molecular weight: 6000)

- Monophenoxypolyethylene glycol($n=6$) methacrylate: commercially available
from Shin-Nakamura Chemical Co., Ltd. under the trade name of NK ESTER
PHE-6G

- Monomethoxypolyethylene glycol($n=4$) methacrylate: commercially available
from Shin-Nakamura Chemical Co., Ltd. under the trade name of NK ESTER
M-40G

[0086]

[Table 1]

Prep. Ex. No.	Initially Charged Monomers [Parts by weight]	Dropping Monomers [Parts by weight]	Weight- Average Molecular Weight
1	Methacrylic Acid [4] Styrene [19.4] Methyl Methacrylate [10] Styrenic Macromer [4] 3-Mercapto-1,2-Propanediol [0.18]	Methacrylic Acid [6] Styrene [28] Methyl Methacrylate [28] 3-Mercapto-1,2-Propanediol [0.32]	17000
2	Acrylic Acid [5] 2-Hydroxyethyl Methacrylate [4] Styrene [25] Styrenic Macromer [8] 6-Mercaptodiglycerol [0.4]	Acrylic Acid [8] 2-Hydroxyethyl Methacrylate [6] Styrene [40] Styrenic Macromer [2] 6-Mercaptodiglycerol [0.6]	19400
3	Acrylic Acid [5] 2-Hydroxyethyl Methacrylate [4] Monomethoxypolyethylene Glycol(n=4) Methacrylate [3] Styrene [22] Styrenic Macromer [8] 1-Thio- β -D-Glucose [0.4]	Acrylic Acid [8] 2-Hydroxyethyl Methacrylate [6] Monomethoxypolyethylene Glycol(n=4) Methacrylate [3] Styrene [37] Styrenic Macromer [2] 1-Thio- β -D-Glucose [0.6]	20500
4	Methacrylic Acid [8] 2-Hydroxyethyl Methacrylate [3] Monophenoxypolyethylene Glycol(n=6) Methacrylate [8] Styrene [23.3] Styrenic Macromer [8] 3-Mercapto-1,2-Propanediol [0.3]	Methacrylic Acid [10] 2-Hydroxyethyl Methacrylate [4] Monophenoxypolyethylene Glycol(n=6) Methacrylate [2] Styrene [30] Styrenic Macromer [2] 3-Mercapto-1,2-Propanediol [0.4]	16000
5	Methacrylic Acid [8] 2-Hydroxyethyl Methacrylate [3] Monophenoxypolyethylene Glycol(n=6) Methacrylate [8] Styrene [23] Styrenic Macromer [8] Dodecyl Mercaptan [0.6]	Methacrylic Acid [10] 2-Hydroxyethyl Methacrylate [4] Monophenoxypolyethylene Glycol(n=6) Methacrylate [2] Styrene [29.6] Styrenic Macromer [2] Dodecyl Mercaptan [0.8]	18500

(Note)

Amounts of each of the components in brackets [] are expressed by parts by weight.

[0087]

Preparation Example 6 (Preparation of Aqueous Dispersion of Hydrophobic Dye-Containing Water-Insoluble Polymer Particles)

A hydrophobic dye shown in Table 2 and 100 g of toluene were added to 28 parts by weight of the polymer solution obtained in Preparation Example 1 (solid content of the polymer: 50% by weight). After the hydrophobic dye was completely dissolved, a neutralizing agent shown in Table 2 was added thereto to neutralize a salt-forming group of the polymer. Two-hundred parts by weight of ion-exchanged water was further added thereto with stirring. Thereafter, the mixture was dispersed with Microfluidizer (commercially available from Microfluidizer Corp.) for 30 minutes.

[0088]

Methyl ethyl ketone, toluene and a part of water were distilled off from the resulting dispersion with an evaporator, to give an aqueous dispersion of hydrophobic dye-containing water-insoluble polymer particles, the solid content of which was 20% by weight. The average particle diameters of the water-insoluble polymer particles contained in the resulting aqueous dispersion were determined on the basis of the following method. The results are shown in Table 2.

[0089]

Incidentally, the coloring material obtained in Preparation Example 6 is an aqueous dispersion of hydrophobic dye-containing water-insoluble polymer particles, since 70% by mole of the methacrylic acid moiety of the polymer contained is neutralized, and the polymer exhibits water insolubility.

[0090]

[Method of Determining Average Particle Diameters of Water-Insoluble Polymer Particles]

The average particle diameter was determined by using a particle size distribution analyzer commercially available from Otsuka Denshi K.K. under the trade name of ELS-8000. As the determination conditions, the temperature of 25°C, the angle between the incident beam and a detector of 90°, the total integrated count of 100 counts, a refractive index (1.333) of water as a refractive index of a dispersing solvent were inputted to the particle size distribution analyzer. As a standard substance, one commercially available from Seradyn under the trade name of Uniform Microparticles (average particle diameter: 204 nm) was used.

[0091]

Preparation Examples 7 to 10 (Preparation of Aqueous Dispersion of Pigment-Containing Water-Insoluble Polymer Particles)

A pigment, methyl ethyl ketone, ion-exchanged water and a neutralizing agent listed in Table 2 were added to 28 parts by weight of the polymer solution (solid content of the polymer: 50% by weight) obtained in Preparation Examples 2 to 5, and the resulting mixture was sufficiently stirred. Thereafter, the mixture was kneaded twenty times with a triple-roll mill (commercially available from NORITAKE CO., LIMITED under the trade name of NR-84A).

[0092]

The resulting paste was added to 250 parts by weight of ion-exchanged water, and the mixture was sufficiently stirred. Thereafter, methyl ethyl ketone and water were distilled off using an evaporator, to give an aqueous dispersion of pigment-containing water-insoluble polymer particles, the solid content of which

was 20% by weight. The determination results for the average particle diameter of the resulting aqueous dispersion of the pigment-containing water-insoluble polymer particles are shown in Table 2.

[0093]

Each name listed in Table 2 means the followings:

- Magenta dye: commercially available from Orient Chemical Co., Ltd. under the trade name of Oil Pink 312
- Carbon black: commercially available from Degussa under the trade name of Color Black FW18
- Cyan pigment: commercially available from DAINIPPON INK & CHEMICALS, INC. under the trade name of Fastogen Blue TGR-SD

[0094]

[Table 2]

Prep. Ex. No.	Polymer	Pigment/Dye	Methyl Ethyl Ketone	Ion-Exchanged Water	Neutralizing Agent	Average Particle Diameter (nm)
6	Prep. Ex. 1	Magenta Dye [14]	[126]	[200]	30% Aqueous NaOH [1.5]	110
7	Prep. Ex. 2	Cyan Pigment [21]	[30]	[5]	30% Aqueous NaOH [2.4]	121
8	Prep. Ex. 3	Cyan Pigment [21]	[30]	[5]	30% Aqueous NaOH [2.4]	115
9	Prep. Ex. 4	Carbon Black [26]	[30]	[5]	30% Aqueous NaOH [2.7]	132
10	Prep. Ex. 5	Carbon Black [26]	[30]	[5]	30% Aqueous NaOH [2.7]	136

(Note)

Amounts of each of the components in brackets [] are expressed by parts by weight.

[0095]

Examples 1 to 4

There were mixed together 20 parts by weight of the aqueous dispersion of colorant-containing vinyl polymer particles obtained in Preparation Examples 6 to 9, 8 parts by weight of glycerol, 5 parts by weight of polyethylene glycol (molecular weight: 800), 0.2 parts by weight of acetylene glycol-polyethylene oxide adduct (commercially available from Kawaken Fine Chemicals Co., Ltd. under the trade name of Acetylenol EH) and 66.8 parts by weight of ion-exchanged water. The resulting liquid mixture was filtered with a membrane filter (commercially available from Fuji Photo Film Co., Ltd., under the trade name of Disc Capsule CALC120 2.5CMD 50) having a pore diameter of 1.2 μm , to give water-based inks.

[0096]

Example 5

There were mixed together 10 parts by weight of the polymer emulsion obtained in Preparation Example 4 not containing a colorant (aqueous dispersion in which 70% by mole of methacrylic acid of the polymer was neutralized, a solid content of which is 20% by weight, average particle diameter: 140 nm), 26 parts by weight of self-dispersible carbon black (aqueous dispersion, solid content of which is 15% by weight, commercially available from Cabot Corporation under the trade name of CAB-O-JETTM300), 8 parts by weight of glycerol, 5 parts by weight of polyethylene glycol (molecular weight: 800), 0.2 parts by weight of acetylene glycol-polyethylene oxide adduct (commercially available from Kawaken Fine Chemicals Co., Ltd. under the trade name of Acetylenol EH) and 50.8 parts by weight of ion-exchanged water. The resulting

liquid mixture was filtered with a membrane filter (commercially available from Fuji Photo Film Co., Ltd., under the trade name of Disc Capsule CALC120 2.5CMD 50) having a pore diameter of 1.2 μm , to give a water-based ink.

[0097]

Comparative Example 1

The same procedures as in Example 1 were carried out except that the aqueous dispersion of colorant-containing vinyl polymer particles in Example 1 was changed to the aqueous dispersion of water-insoluble polymer particles obtained in Preparation Example 10, to give a water-based ink.

[0098]

Next, the physical properties of the water-based inks obtained in each of the Examples and the Comparative Example were determined on the basis of the following methods. The results are shown in Table 3.

[0099]

(1) Jetting Property and Blotting Resistance of Water-Based Ink

Continuous printing was carried out on 10 sheets of Canon PB paper at 2000 characters per sheet by using a bubble jet printer (registered trademark) commercially available from CANON INC. under the product number of "F870". Thereafter, a test document including characters, solid images and ruled lines was printed on the paper, and the jetting property was evaluated. The evaluation criteria are as follows:

[0100]

[Evaluation Criteria]

◎: Satisfactory in all of three items of sharp and clear characters, uniform solid images and no crookedness of printed ruled lines (no problem in actual use)

○: Almost satisfactory in three items of sharp and clear characters, uniform solid images and no crookedness of printed ruled lines (no problem in actual use)

×: Unsatisfactory in at least one of three items of sharp and clear characters, uniform solid images and no crookedness of printed ruled lines (problem in actual use)

[0101]

(2) Water Resistance

Solid image printing was carried out by using the printer and the paper mentioned above, and the paper was allowed to stand in the air at 25°C for 1 hour. Thereafter, the printed copy paper was immersed vertically in stand-still water for 10 seconds, and the paper was vertically lifted therefrom. After drying the paper in the air at 25°C, the optical density was determined. The residual ratio of the optical density after immersion to the optical density immediately after solid image printing was obtained. The water resistance was evaluated on the basis of the following evaluation criteria:

[0102]

[Evaluation Criteria]

◎: Residual ratio being at least 95%

○: Residual ratio being at least 90% and less than 95%

△: Residual ratio being at least 70% and less than 90%

×: Residual ratio being less than 70%.

[0103]

(3) High Lighter-Fastness

Text printing was carried out by using the printer and the paper used mentioned above. After 6 hours passed, the extent of staining of the printed

sample when traced with a commercially available aqueous fluorescent marker (commercially available from PILOT CORPORATION, under the trade name of "Spotliter V" OA SGV-15SL) was observed with naked eyes, and the evaluation was made on the basis of the following evaluation criteria:

[0104]

[Evaluation Criteria]

- ◎: No staining such as rubbed stains was observed even when traced with a fluorescent marker.
- : Some rubbed stains which would cause no problem in practical use were generated when traced with a fluorescent marker.
- ×: Generation of rubbed stains were observed when traced with a fluorescent marker, which was intolerable.

[0105]

(4) Rubbing Resistance

Solid image printing was carried out on a gloss paper (commercially available from SEIKO EPSON CORPORATION under the trade name of MC gloss paper) by using the above-mentioned printer. After 6 hours passed, the printed surface was strongly rubbed with a finger. The extent of rub-off of the printed image was evaluated on the basis of the following evaluation criteria:

[0106]

[Evaluation Criteria]

- ◎: Substantially no printed image being rubbed off, and its periphery being not stained.
- : Some printed images being rubbed off, and its periphery being stained a little which would cause no problem in actual use.

×: Printed images being considerably rubbed off, its periphery being drastically blacked, and finger also being considerably stained.

[0107]

[Table 3]

Ex. No.	Kind of Coloring Material	Jetting Property and Blotting Resistance	Water Resistance	High Lighter -Fastness	Rubbing Resistance
1	Prep. Ex. 6	○	◎	◎	◎
2	Prep. Ex. 7	○	◎	◎	○
3	Prep. Ex. 8	◎	◎	◎	○
4	Prep. Ex. 9	◎	◎	◎	○
5	Prep. Ex. 4	◎	◎	○	○
Comp. Ex. 1	Prep. Ex. 10	×	◎	◎	○

(Note)

Preparation Example No. listed in the column of "Kind of Coloring Material" means the coloring material used in each of the Examples or the Comparative Example.

[0108]

It can be seen the results shown in Table 3 that the water-based ink obtained in each of the Examples is excellent in jetting property, blotting resistance, water resistance, high-lighter fastness and rubbing resistance.

[0109]

[Effects of the Invention]

The water-based ink of the present invention is excellent in water resistance, high-lighter fastness and rubbing resistance, and also excellent in jetting property and blotting resistance when printed with an inkjet printer.

[Document] Abstract

[Abstract]

[Problems]

To provide a water-based ink which is excellent in water resistance, high-lighter fastness and rubbing resistance, and also excellent in jetting property and blotting resistance when printed with an inkjet printer.

[Solving Means]

A water-based ink containing a colorant and a water-insoluble polymer having at least two hydroxyl groups at its end.

[Selected Drawings] None

BACKGROUND INFORMATION OF APPLICANT

Identification Number

[000000918]

1. Date of Conversion

August 24, 1990

[Reason for Conversion]

New Registration

Address

14-10, 1-chome, Kayaba-cho, Nihonbashi,

Chuo-ku, Tokyo

Name

Kao Corporation